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Sugarcane and pinewood biochar effects on activity and aerobic soil dissipation of metribuzin and pendimethalin

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ABSTRACT

Biochars were produced by pyrolysis of sugarcane bagasse (350 °C and 700 °C) and pine wood (400 °C) and are abbreviated BC350, BC700, and WC400, respectively. Metribuzin adsorption by batch equilibrium showed that BC700 had the greatest adsorption capacity followed by BC350 and WC400. The bagasse biochars were mixed with clay and a silt loam soil and the pine wood biochar with a loamy sand soil and fortified with the metribuzin and pendimethalin. The soils were incubated at 25 °C in the dark and were extracted with methanol after 0, 7, 14, 21, 28, 42, 63, 86, and 111 days. Parent compounds and metribuzin degradates were analyzed in extracts by HPLC – mass spectrometry. Increases in metribuzin half life (DT_{50}) were indicated for all soil-biochar combinations. BC350 had the greatest impact, doubling the DT_{50} in the silt loam soil. In contrast, BC700 had minimal impact on the DT_{50} in the silt loam soil and contributed to a significant DT_{50} decrease in the clay. The metribuzin degradate, metribuzin-desamino, was detected at rates proportional to metribuzin dissipation. For pendimethalin, biochar additions increased DT_{50} in all soil-biochar combinations. In contrast to metribuzin, BC700 and WC400 had the greatest impact with the BC700 increasing the DT_{50} more than 2-fold. In the loamy sand soil, the 1–4% biochar rate contributed to an increased trend in palmer amaranth emergence. At the 8% rate, palmer amaranth emergence was statistically higher than the control ($p = 0.072$). In sum, how biochar impacted the activity and dissipation of these herbicides depended on soil, herbicide, and biochar properties.

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1. Introduction

Biochars produced from pyrolysis of crop residues, mill by-products, fermentation wastes, and municipal solids have been identified as soil amendments that may improve soil quality (Laird, 2008; Lehmann et al., 2006). Potential positive impacts include increased soil organic matter (SOM), more permanent soil carbon (C) sequestration, increased herbicide persistence, and improved soil physical properties (Laird, 2008). Negative impacts may include herbicide carryover and reduced efficacy, increased availability for runoff, and lower crop nutrient availability (Verheijen et al., 2009). Biochar properties vary depending on parent material and pyrolysis temperature. In turn this has been shown to control its impact on soil properties and processes (Verheijen et al., 2009).

Many crops, such as sugarcane (*Saccharum* sp.) and peanut (*Arachis hypogaea*), do not have herbicide-resistant varieties. Additionally, glyphosate-resistant weed species (e.g., *Amaranthus palmeri*) emergence has increased in cropping systems of Southeastern USA (Culpepper et al., 2006). Soil residual preemergence herbicides are now more widely used in these systems to control weeds. Two examples are metribuzin (4-amino-6-*tert*-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one) and pendimethalin (*N*-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine). The herbicides target germinating broadleaf and grass weed species. Metribuzin is relatively water soluble and has a lower affinity to bind to soil organic materials. Pendimethalin, on the other hand, is highly insoluble and binds strongly to soil organic materials (Footprint, 2013). Integrating a soil amendment such as biochar into these cropping systems requires knowledge on how it will affect the environmental fate and activity of soil applied herbicides, including increasing the residual and/or lowering efficacy through sorption and other mechanisms.

To date several studies have measured the partitioning of herbicides and insecticides to biochar-amended soil, biochar itself, and charcoal and evaluated potential impacts on soil dissipation rates

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Table 1
Properties of the soils used in the laboratory incubation study.

Soil Series	Location, crop	pH (1:1)	CEC ($cmol_c\ kg^{-1}$)	SOC (%)	TN (%)	P ($mg\ kg^{-1}$)	K ($mg\ kg^{-1}$)	Ca ($mg\ kg^{-1}$)	Na ($mg\ kg^{-1}$)
Tifton fine loamy sand	Georgia, peanut/cotton	6.8	8.0	0.78	0.06	55	112	977	33
Cancienne silt loam	Louisiana, sugarcane	6.0	16	0.85	0.08	29	81	1512	28
Schriever clay	Louisiana, sugarcane	6.1	34	1.20	0.12	49	294	3604	43

(Mesa and Spokas, 2011). For example, fluometuron and 4-chloro-2-methylphenoxyacetic acid (MCPA) both partitioned to soil more strongly when the soil was amended with wood biochars (Cabrera et al., 2011). Diuron and pyrimethanil also sorbed more strongly to soil amended with biochars (Yu et al., 2010, 2006). These chemicals range in water solubility from 40 $mg\ L^{-1}$ (diuron) to 29,000 $mg\ L^{-1}$ (MCPA) (Footprint, 2013). Biochars derived from red gum wood (*Eucalyptus* spp.) increased the half life (DT_{50}) of carbofuran and chlorpyrifos in soil by up to 30 d (Yu et al., 2009), and doubled the DT_{50} of pyrimethanil in three agricultural soils (Yu et al., 2011). Conversely, hardwood biochar amendment up to 5% by weight to soil did not reduce mineralization of atrazine in atrazine-adapted soil (Jablonowski et al., 2013). However, deisopropylatrazine, a by-product of atrazine dissipation, strongly sorbed onto biochars made from cotton mill waste and flax shive (Uchimiya et al., 2012).

Pyrolysis temperature creates distinct biochars that display variable characteristics relating to sorption (Sun et al., 2011). Atomic ratios related to polarity [(O + N)/C] decreased from 0.73 to 0.12 as pyrolysis temperature increased from 100 °C to 600 °C, with a concomitant increase in surface area from 2.1 to 330 $m^2\ g^{-1}$ (Zhang et al., 2011; Chen et al., 2008). The log K_{oc} of simazine determined in batch experiments with corn straw biochar increased from 2.2 (biochar pyrolysis temperature 100 °C) to 4.9 (biochar pyrolysis temperature 600 °C) (Zhang et al., 2011). A lower pyrolysis temperature (250 °C vs. 650 °C) resulted in higher dissolved organic carbon (DOC) leaching from oak (*Quercus lobata*) and Gamma grass (*Tripsacum floridanum*) biochar amended soils (Mukherjee and Zimmerman, 2013). Singh et al. (2012) found increasing pyrolysis temperature from 400 °C to 550 °C extended biochar recalcitrant carbon DT_{50} from 150 to 500 y. And Luo et al. (2013) found higher microbial usage of biochar C when pyrolysis temperature was lower (350 °C vs. 700 °C). Thus low when compared to high temperature biochars can be described as products that have lower sorption capacity for herbicides and other organic compounds and are more labile, possibly influencing microbial processes to a greater extent than less-labile, more carbonized, higher temperature biochars.

Given these differences, testing of regionally available feedstocks for biochar production is important to evaluate biochar for agricultural uses. A potential feedstock in south Louisiana is sugarcane bagasse. The Louisiana sugarcane industry produced 14 million tons of cane in 2012 (K. Gravois, personal communication, 2013). A significant amount of bagasse remained and could be used as a pyrolysis feedstock. Biochar yield was 31%, syngas energy produced was 1.4 $MWh\ t^{-1}$, and electricity produced was 0.5 $MWh\ ton^{-1}$ for dry bagasse (Quirk et al., 2012). In other parts of the southeastern USA residues generated by the forest products industry are abundant. For example, in Georgia, commercial forests produce 19 million more tons than are harvested each year (Georgia Forestry Commission, 2010). Our hypothesis is that if herbicide sorption is related to biochar surface area, increasing the surface area will increase herbicide sorption. Thus, our first objective was to determine the impact of differing biochars on soil dissipation of two common soil-applied preemergence herbicides. Our second hypothesis is that if herbicides are sorbed onto biochars, higher rates of biochar will result in higher rates of herbicide sorption. Our second objective was to evaluate different rates of biochar on the adsorption of herbicides by conducting a greenhouse weed germination study.

2. Materials and methods

2.1. Soil collection and characterization

Surface samples (0–15 cm) of Cancienne silt loam (Fine-silty, mixed, superactive, nonacid, hyperthermic Fluvaquentic Epiaquepts) and Schriever clay (Very-fine, smectitic, hyperthermic Chromic Epiaquerts) were collected from the USDA-ARS Sugarcane Research Unit's Ardoyne Farm in Schriever, LA (29°38′09.37″ N, 90°56′25.79″ W). Tifton loamy sand (Fine-loamy, kaolinitic, thermic Plinthic Kandiudults) was collected from the University of Georgia's Gibbs Farm near Tifton, GA (31°26′12.51″ N, 83°35′16.96 W). All soil was sieved to pass 2-mm screen and stored at room temperature in field moist condition. Soil pH was measured with an electrode in a 1:1 soil:water slurry (Thomas, 1996). Soil organic C and total N were analyzed by dry combustion on a Shimadzu TOC-V CPN analyzer (Colombia, MD, USA) with an autosampler and a TNM-1 nitrogen unit (Nelson and Sommers, 1996). Mehlich III extractable potassium (K), phosphorous (P), calcium (Ca), sodium (Na) were analyzed using inductively coupled plasma (ICP) spectroscopy (Helmke and Sparks, 1996). Soil CEC was obtained by summing the positively charged cations (Sumner and Miller, 1996). Soil properties are listed in Table 1.

2.2. Biochar characterization

Pine wood-derived biochar was obtained from Dr. Brian Baldwin from Mississippi State University in Starkville, MS. The two sugarcane bagasse biochars were produced from pelletized sugarcane bagasse donated by Raceland Raw Sugars in Raceland, LA. The bagasse pellets were ground using a Jeffco mill (Bisbane, Queensland, AUS), sieved to pass a 2-mm screen, and slow pyrolyzed at 350 °C or 700 °C for 1 h. The 350 °C bagasse biochar (BC350) was dark brown in color and resembled the plant material from which it was derived. The pine wood (WC400) and 700 °C bagasse (BC700) biochars were both black in color and resembled fine charcoal. To assess potential for leaching dissolved organic carbon (DOC) and nitrogen (TN) one gram of each biochar was shaken in 20 mL of 0.01 M $CaCl_2$ overnight. The filtrate was analyzed for DOC and TN on as listed above. The procedure was repeated in triplicate. The DOC and TN values were summed. Biochar pH was determined on a 1:100 biochar:water solution after agitation for 72 h using an electrode. Biochar surface area was measured by nitrogen adsorption isotherms at 77 K using NOVA 2000 surface area analyzer (Quantachrome, Boynton Beach, FL, USA) according to Uchimiya et al., 2011. Elemental composition (OC, ON, S) was determined by dry combustion using PerkinElmer 2400 Series II CHNS/O analyzer (PerkinElmer, Shelton, CT, USA). Total P, total K, and total S were analyzed by digesting biochar in a microwave digestion system with concentrated hydrochloric and nitric acid, and hydrogen peroxide, diluted and analyzed by ICP spectroscopy (Lima et al., 2014). Physical and chemical characteristics of the biochars are described in Table 2. Ash content was determined in triplicate by following American Society for Testing and materials (ASTM) method D5142 using a LECO thermogravimetric analyzer (TGA701, LECO, St. Joseph, MI, USA) by proximate analysis where sample is heated at 650 °C under O_2 atmosphere in an open crucible until sample weight stabilizes.

Table 2
Characteristics of biochars used in the experiment.

Abbreviation	WC400	BC350	BC700
Biomass source	Yellow pine chipped	Sugarcane bagasse	Sugarcane bagasse
Pyrolysis temperature (°C)	400	350	700
% Yield	Not available	44.9	28.3
Surface area ($m^2\ g^{-1}$)	0.5	2.6	82
Bulk density ($g\ mL^{-1}$)	0.23	0.19	0.23
% Passing 2 mm sieve	>99	96	97
% Passing 1 mm sieve	62	80	88
pH (in water)	5.96	4.96	8.66
% Organic carbon	71 ± 3.8	57 ± 1.5	70 ± 1.3
% Organic nitrogen	0.1 ± 0.004	0.34 ± 0.01	0.4 ± 0.004
P ($mg\ g^{-1}$)	0.17	0.58	0.92
S ($mg\ g^{-1}$)	0.1	0.32	0.27
K ($mg\ g^{-1}$)	1.77	4.79	7.02
DOC ($mg\ g^{-1}$)	2.32	3.78	0.18
DON ($mg\ g^{-1}$)	0.01	0.07	0.01

2.3. Sorption study

Metribuzin sorption on the biochars was evaluated by batch equilibrium. Twenty milliliters of solutions containing 0.1, 0.25, 0.5, 1.25, 2.5, 5, 7.5, 12.5, and 25 $\mu g\ mL^{-1}$ metribuzin in 0.01 M $CaCl_2$ were combined with biochars in 30 mL screw-cap Teflon FEP centrifuge tubes (ThermoFisher Scientific, Pittsburgh, PA, USA). Biochar additions were WC400, 0.4 g, BC350, 0.2 g, and BC700, 0.1 g. Biochar amounts used were based on a preliminary study which identified the quantity needed to reduce the metribuzin solution concentration by at least 20%. After shaking overnight at 25 °C, tubes were centrifuged at 3000 g and 5.0 mL of the supernatant was filtered through a 0.2 micron Supor® membrane syringe filters (Pall Corp., Ann Arbor, MI, USA). Filtrates were analyzed directly by LC–MS using analytical conditions described below.

2.4. Soil dissipation study and pesticide residue analysis

Reagent grade metribuzin and pendimethalin were purchased from Chem Service Inc. (West Chester, PA, USA), dissolved in acetone (HPLC grade), and combined with dry fine (60 mesh) sand. After evaporation of the acetone overnight, the sand and pesticides were ground with a mortar and pestle. Metribuzin and pendimethalin were chosen for study based on their extensive usage in regional cropping systems and for their wide varying water solubility and K_{oc} values (Fig. 1).

Fifty grams (dry weight equivalent) of soils were placed in 250-mL square glass bottles and soil water content adjusted with deionized water to bring soil moisture to field capacity – 0.12, 0.19, and 0.21 g water g^{-1} soil for the loamy sand, silt loam, and clay soils, respectively. The BC350 and BC700 were added to the clay and silt loam soils and the WC400 to the loamy sand, all at a 2% rate (1 g $bottle^{-1}$). Bottle contents were then mixed by shaking. Pesticide fortified-sand was added at a rate of 0.1 g $bottle^{-1}$ to every bottle, and entire contents mixed again by shaking. The sand addition was equivalent to 3.0 and 2.8 kg a.i. ha^{-1} for metribuzin and pendimethalin, respectively. There were 27 bottles for each soil + biochar mixture, including controls without biochar. All bottles were sealed with Teflon lined screw caps and incubated in the dark at 25 °C. At 0, 7, 14, 21, 28, 42, 63, 86, and 111 d, 50-mL of methanol was added to 3 replicate bottles from the control and each treatment group. These bottles were then re-capped, shaken, and stored in a −20 °C freezer. A subset of each soil and biochar mixture was analyzed for total C by dry combustion.

At end of the incubation, all frozen bottles were brought to room temperature, mechanically shaken for 1 h at 220 rpm, allowed to settle, and methanol recovered by vacuum filtration (Whatman GFF filter). The procedure was repeated with two additional 50-mL methanol aliquots. Extracts were combined, and concentrated to 10 mL under a stream of N_2 gas at 50 °C. Extracts were fortified with 2-chlorolepidine (internal standard), and analyzed by HPLC–MS with a Thermoquest-Finnegan LCQ DECA ion trap system (Thermo-Fisher Scientific, San Jose, CA, USA). Metribuzin and pendimethalin were analyzed using atmospheric pressure chemical ionization with a Gemini® C18HPLC column, 150 × 4.6 mm, 0.5 um, 110 Å (Phenomenex, Torrance, CA, USA). Methanol (A) and 0.1% formic acid (B) elutions were made at 1 mL^{-1}. Initial conditions 10% A/90% B were changed to 90% A/10% B over 9 min, held for 5 min, and returned to initial conditions in 1 min. The base-peaks in the metribuzin and pendimethalin full scan (100-450 m/z) mass spectra, $m/z^+ = 215$ and 282, respectively, representative each of the $(M+H)^+$ ion, were used for quantification. Comparison of samples frozen at time = 0 with initial sand spikes indicates that 68 and 50% of metribuzin and pendimethalin was recoverable from soil. Biochar caused a slight reduction in the recovery of metribuzin (68 vs. 63%) but did not affect pendimethalin recovery. Degradation products of metribuzin, metribuzin-diketo (DK), metribuzin-desamino (DA), and metribuzin-desamino-diketo (DADK) were purchased from Dr. Ehrenstorfer Analytical Standards (Augsburg, GER). These compounds were detected using electrospray ionization in the negative ion mode. Base peaks in spectra were equivalent to $(M-H)^-$. They were used for quantification.

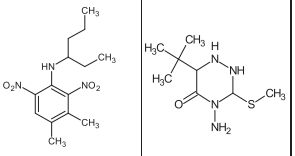
Trade	Prowl	Sencor
Common	Pendimethalin	Metribuzin
Class	dinitroanilide	triazinone
MOA	Cell/Root inhibitor	PSII inhibitor
Chemical structure		
S_w ($mg\ L^{-1}$)	0.33	1165
KOC ($ml\ g^{-1}$)	15744	38

Fig. 1. Chemical properties and structures of soil-applied herbicides, metribuzin and pendimethalin, used in the study. MOA is mode of action; K_{oc} is organic carbon partition coefficient.

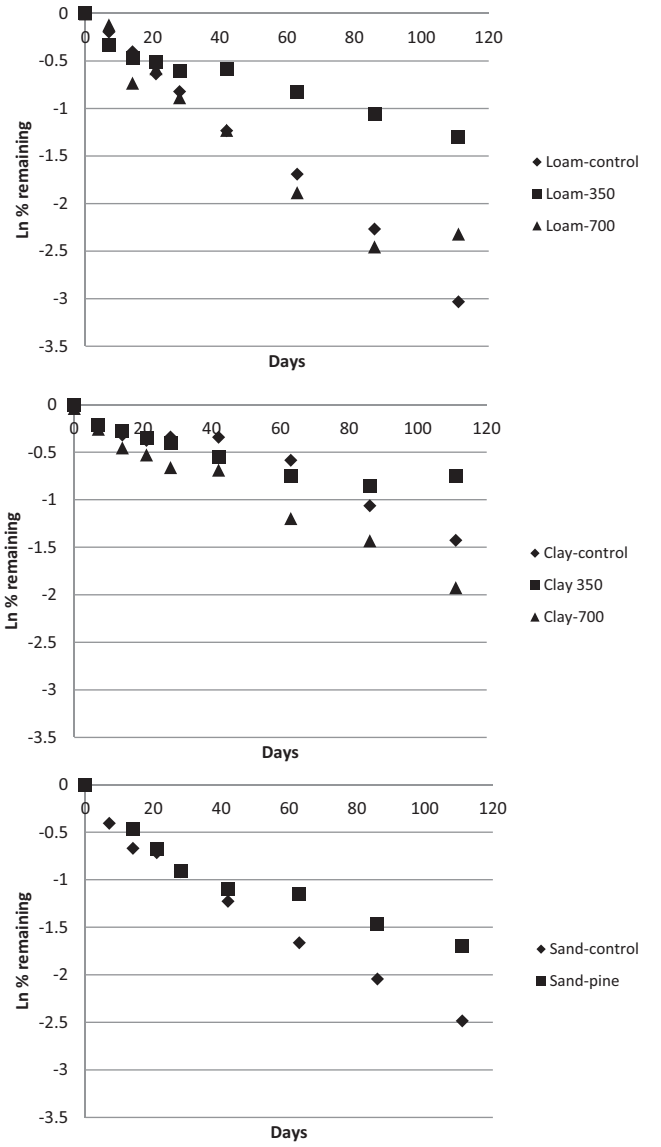


Fig. 2. Natural log of the % metribuzin remaining over time in (A) silt loam soil, (B) clay soil, and (C) sand soil both with and without additions of either sugarcane bagasse biochar (A and B) or pine wood biochar (C). Data points are means of three replicates. These data were used in the ANOVA to evaluate treatment mean (DT_{50}) differences.

2.5. Greenhouse pesticide efficacy study

A greenhouse efficacy trial was conducted to determine if the biochars would interact with soil and herbicides to affect herbicide efficacy. Palmer amaranth (*Amaranthus palmeri*) seed was obtained from Dr. Caleb Dalley (USDA-ARS) and was tested for germination by placing 15 seeds of each into four petri dishes between sheets of moist filter paper. Germination was found to be 100%. The test was conducted in the greenhouse at ambient temperatures (>16 °C) and germination was indicated by radical emergence. Tifton loamy sand or Cancienne silt loam was air-dried and weighed into 15-cm diameter plastic pots. The WC400 and BC700 were added at rates of 0–2, 4, and 8% by weight. Four replications of each treatment combination were used for the greenhouse study. Pots were watered to saturation and allowed to drain by gravity. This was repeated daily to promote germination of any weed seeds present. Indigenous weeds which germinated over a period of two weeks were physically removed. Fifteen palmer amaranth seeds were then sowed about 1 cm beneath the soil surface in each pot. Fifty ml of an aqueous solution containing pendimethalin (Prowl® H_2O) and metribuzin (Sencor® 75DF) at 0.56 and 0.28 kg ha^{-1} was added to each pot and allowed to soak into the soil. Counts of germinating palmer amaranth seedlings were taken at 3 d intervals for 2 w.

Table 3
Parameters obtained by fitting metribuzin adsorption data to Freundlich and linear models.

Abbreviation	WC400	BC350	BC700
Freundlich equation fit			
K_f	3.37	9.77	47.2
b	1	0.93	0.61
R^2	0.993	0.987	0.996
Linear fit			
k_d	3.35	8	15.9
R^2	0.999	0.991	0.946
K_{foc}	5	17	67
K_{oc}	5	14	23

K_f = sorption parameter (mg kg^{-1}/mg L^{-1}).
b = exponent index.
K_d = sorption coefficient (L kg^{-1}).
K_{foc} = carbon normalized K_f (mg kg^{-1} OC/mg L^{-1}), foc = %C in biochar.
K_{oc} = organic carbon normalized sorption coefficient (L kg^{-1} OC).

2.6. Data analysis

Dissipation data were fit to a first-order kinetic equation by linear regression of time and the natural log of the % herbicide remaining and analyzed by 1-way ANOVA with pairwise comparisons of regression slopes made using Fishers LSD in GraphPad Prism version 6 (La Jolla, CA, USA). Half life (DT_{50}) of pesticides was calculated based on regression coefficients obtained using the equation $DT_{50} = 0.693/k$ (dissipation coefficient). Means were separated statistically at the $p < 0.05$ level. Pair-wise statistical differences (p-values) between DT_{50} are indicated in the text. Soil C and palmer amaranth germination data were analyzed using PROC MIXED with soil and biochar as fixed variables and replication as a random variable using SAS version 9 software (SAS Institute, Cary, NC, USA). Means of significant effects were separated using the PDIFF option with the SAXTON macro at the $p = 0.10$ level (Saxton, 1998).

3. Results and discussion

3.1. Metribuzin sorption onto biochars

Adsorption isotherms were evaluated via the Freundlich and a linear model. For the linear model, K_d (sorption coefficient) = C_s/C_w, where C_s is the concentration sorbed (μg g^{-1}), C_w is the concentration in aqueous solution (μg mL^{-1}). The Freundlich model was $C_s = K_f{}^* C_w{}^b$ where K_f is the Freundlich sorption coefficient, and b is the exponent index. The data fit both models well with $R^2 > 0.95$ (Table 3). The Freundlich sorption coefficient (K_f) for the BC700 was 4.8X and 14X greater than BC350 or WC400 values, respectively. The BC700 Freundlich exponent, 0.61, also indicated non-linear adsorption. K_f values increased with the same trend as biochar surface area, which for the BC700 char were 31X and 170X greater than the BC350 or WC400 biochars, respectively (Table 3). The trend to non-linear adsorption and increased adsorption capacity as indicated increases in the Freundlich coefficient, K_f, as biochar pyrolysis temperature was increased has been reported in numerous other studies (Mesa and Spokas, 2011). The K_d values obtained by fitting data to the linear model the same trend (Table 3). K_{oc} and K_{foc} were computed by dividing corresponding values by biochar fraction organic carbon. Results again showed that BC700 had the greatest adsorption capacity since this material had substantially

Table 4
Soil dissipation rate constants (K) and half life (DT_{50}) for metribuzin and pendimethalin.

		Metribuzin		Pendimethalin	
Soil	Biochar	K (day^{-1})	DT_{50}	K (day^{-1})	DT_{50}
Cancienne silt loam	Control	0.027	25	0.031	23
	350 °C bagasse	0.013	54	0.019	36
	700 °C bagasse	0.026	27	0.013	54
Schriever clay	Control	0.012	57	0.031	22
	350 °C bagasse	0.009	74	0.023	31
	700 °C bagasse	0.018	39	0.013	52
Tifton loamy sand	Control	0.025	28	0.028	25
	Pine wood	0.018	39	0.017	41

higher K_{oc} and K_{foc}. The BC700 values were within the range of values reported for soil organic matter (Footprint, 2013) reflecting the biochar's relatively high surface area and capacity to adsorb non-polar organic compounds like metribuzin.

3.2. Metribuzin dissipation

In controls metribuzin dissipated more slowly in the Schriever clay (DT_{50} = 57 d) than either the Cancienne silt loam (DT_{50} = 25 d) or the Tifton loamy sand (DT_{50} = 28 d) (Fig. 2, Table 4). The clay soil had 1.6X–2X more SOC (Table 2) which may have increased metribuzin persistence through sorption. The smectitic clays present in this soil may also have contributed to the higher metribuzin DT_{50} through processes such as electron-donor complexes, or interact with exchange cations via a water bridge (Sheng et al., 2001). The interaction between clay minerals and organic matter may also be important. Smectitic clays exhibit high surface areas ($680 \pm 100\ m^2\ g^{-1}$) but varied in their sorption characteristics for another triazine herbicide, atrazine (Laird et al., 1992). It is also possible that higher levels of SOC coating a larger mineral surface area in the clay soil increased metribuzin adsorption and reduced its bioavailability thus DT_{50} was greater.

Comparisons to controls showed that BC350 addition to the Cancienne silt loam increased metribuzin DT50 more than 2-fold (Table 4). In contrast data indicated that metribuzin dissipation was not impacted by addition of BC700 (Table 4). Calculated DT_{50} for the control and BC700 amended soil were 25 and 27 d, respectively. The BC350, metribuzin DT_{50} (54 d), was significantly greater than either the control ($p = 0.020$) or the BC700 ($p = 0.022$) values. Addition of BC350 to the Schriever clay and W400 to the Tifton loamy sand also increased metribuzin DT_{50} but the magnitude increases, 1.3 to 1.4-fold, compared to controls were less than observed in the silt-loam soil and were not significant.

In the case of the BC700 addition to the Schriever clay, a significant decrease in metribuzin DT_{50} from 57 (control) to 39 d ($p = 0.030$) was observed. Batch equilibrium studies showed that BC700 had much higher metribuzin adsorption capacity (Table 3). However results showed that the increased potential for adsorption did not substantially decrease metribuzin's bioavailability. This was due in part to the fact that metribuzin exhibited relatively low adsorption on the biochars and soil K_{oc} data indicate that adsorption is relatively weak low on soil organic matter (Footprint, 2013). It is also possible when BC700 was mixed with soil its potential for metribuzin adsorption was reduced due to biochar interactions with clay surfaces. More than 50% decrease in diuron and phenanthrene adsorption on biochars was observed when they were mixed at 0.1% in soil. (Yang and Sheng, 2003; Chen and Yuan, 2011). We do not have an explanation of why a 50 decrease was observed when BC700 was added to the clay. One possibility is the impact alkaline ash mixed with the BC700 biochar increased soil pH and enhanced soil conditions for metribuzin degradation. Ash content values for BC700 were 20.3%, significantly higher than those for BC350 (12.9%) or WC400 (0.88%). The presence of the ash was inferred from the relatively high pH measured with the ash was mixed with water (Table 2). Increasing pH has been reported to decrease metribuzin adsorption by soil and increase degradation rates (Ladlie et al., 1976).

Our original hypothesis was that biochar additions would minimally affect metribuzin dissipation due to its relatively high water solubility and low K_{oc}. The BC700 performed in this manner. However the BC350 increased the metribuzin DT_{50} in both soils to which it was added. One possible cause of the slower dissipation was the much greater amount of DOC that this biochar contributed to soil. This was indicated by leaching 1 g of the biochars sequentially with three 20-mL aliquots of 0.01 M $CaCl_2$ and measuring DOC. The BC350 yielded 3.78 mg DOC g^{-1} char, compared with 2.32 for the WC400 and 0.02 for the BC700. Singh et al. (2012) found that increasing production temperature from 400 °C to 550 °C reduced non-aromatic carbon in wood-derived biochar from 16% to 1.3%.

The added DOC may have been preferentially used as a substrate by soil microorganisms thereby increasing metribuzin persistence. The preferential substrate utilization hypothesis states that if two substances with very different availability are both present in one location, soil microbes will prefer to utilize the more readily available substrate first (Kuzyakov, 2002). The use of the DOC as a substrate could also have limited soil mineral N availability thus slowing microbial metabolism (White et al., 2007). On a mole to mole basis, the DOC in the BC350 added 320 μmol C compared to 1.20 μmol C added with metribuzin. The low SOM in the Cancienne silt loam (1.0%) compared to the Schriever clay soil (1.6%) could have increased the effect. Luo et al. (2013) found similar levels of DOC in *Miscanthus* straw biochar produced at 350 °C (4.43 mg DOC g^{-1} char) and 700 °C (0.3 mg DOC g^{-1} char). They found 20% and <2% of the 350 °C and 700 °C biochar C incorporation into microbial biomass, respectively. Another possibility why BC350 extended metribuzin's dissipation could be the physical properties of the char. Zhang et al. (2013) found chars made from pig manure stock at 350 °C had about 2X the pore volume and pore diameter as chars made at 750 °C. They also found the ratio of O + N/C, an index of polarity, was 2.4X higher in the 350 °C char. The relatively polar metribuzin could migrate into these amorphous pores limiting its bioavailability. However, the sorption data does not strongly support this mechanism in our soil + biochar system (Table 3). With a low surface area ($2.75\ m^2\ g^{-1}$) and relatively low K_d (8.0), metribuzin sorption on BC350 might be secondary, in terms of limiting dissipation, to the high DOC present ($3.78\ mg\ g^{-1}$).

3.3. Pendimethalin dissipation

Pendimethalin dissipation in controls was similar in each soil with an average DT_{50} of 23 d (Table 4). Additions of biochar significantly impacted pendimethalin dissipation. For the silt loam soil, additions of BC350 and BC700 increased DT_{50} by 12 ($p = 0.0012$) and 21 d ($p < 0.0001$), respectively (Fig. 3 and Table 4). The difference between the BC350 and BC700 biochar amended soils was also significant (0.044). The reduced effect of the lower temperature char was similar to the findings of Yu et al. (2009) who observed chlorpyrifos DT_{50} was 12, 16, and 43 d for control soil, soil amended with 1% biochar (production temperature 450 °C), and soil amended with 1% biochar (production temperature 850 °C), respectively. Chlorpyrifos like pendimethalin has relatively high K_{oc} and strong tendency to bind to soil organic carbon (Footprint, 2013). For the clay soil, additions of 350 °C and 700 °C bagasse biochar similarly increased DT_{50} by 9 ($p = 0.031$) and 30 d ($p < 0.0001$), respectively. There was a significant difference between the BC350 and BC700 in the clay soil as well ($p = 0.005$). However, pendimethalin dissipation was similar across both the clay and silt-loam soils (350 vs. 350; 700 vs. 700) with average p-value of 0.572. For the Tifton loamy

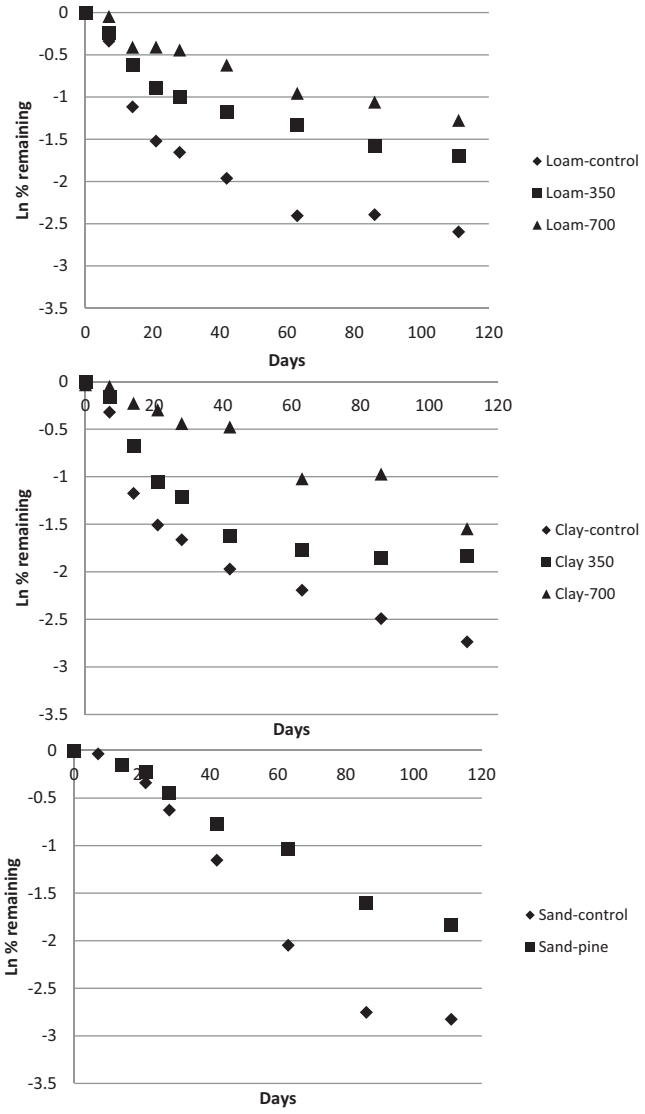


Fig. 3. Natural log of the % pendimethalin remaining over time in (A) silt loam soil, (B) clay soil, and (C) sand soil both with and without additions of either sugarcane bagasse biochar (A and B) or pine wood biochar (C). Data points are means of three replicates. These data were used in the ANOVA to evaluate treatment mean (DT_{50}) differences.

sand, WC400 significantly increased DT_{50} from 25 to 41 d (Fig. 3 and Table 4). The value was intermediate to the effects of the BC350 and BC700 had on clay and silt loam soils. The results were similar to those reported by Yu et al. (2011) who found acetamiprid DT_{50} were increased by biochar additions in loam, silt loam, and sandy soils.

Overall pendimethalin behavior in these agricultural soils was similar to our initial hypothesis: additions of biochar to agricultural soil would increase the dissipation time of agrichemicals. One explanation for the observed pendimethalin behavior was its much lower water solubility and higher K_{oc}, when compared to metribuzin (Fig. 1). The biochar added significant amounts of C to each of the soils (Table 4). For the silt loam, biochar increased measured SOC by over 2.4X; for the clay, biochar increased SOC by over 1.9X; and for the sand, biochar increased SOC by 3.1X. However, Spokas et al. (2009) found that biochar C was not as effective as a sorbent as other forms of soil C for acetochlor and atrazine. For metribuzin K_d's on the biochars were 3.3, 7.8, and 15.9, respectively, for the WC400, BC350, and BC700. Thus it is reasonable to speculate that pendimethalin K_d would display similar sorption differences, i.e., increased surface area would result in increased sorption. The lack of effect of clay on pendimethalin dissipation may be related to the more preferred sorption onto SOC or biochar surfaces. Yu et al. (2011) showed increased acetamiprid sorption coefficients (K_d) for a loam, a silt loam, and a clay soil amended with 0.5% biochar. Yang and Sheng (2003) showed rice and wheat ash were exceptional sorbents for diuron, when compared to soil or crop residue. Biphenyl, which has a water solubility slightly higher than pendimethalin, was shown to prefer organic to mineral complexes by a ratio of 124:1 (Sheng et al., 2001). The increase in pendimethalin DT_{50} between BC350, WC400, and BC700 could also be related to the aromatic content created by pyrolysis at higher temperatures, as several studies have reported aromatic carbon increasing at higher pyrolysis temperature (Masiello, 2004; Hedges et al., 2000). Keiluweit et al. (2010) characterized wood and grass based biochars at increasing charring temperatures from 300 °C to 700 °C and determined both significant increases in fixed carbon content (28.2–92% for wood and 36.2–71.6% for grass) as well corresponding significant decreases in H/C ratios (1.42–0.21 for wood and 1.34–0.20 for grass). Both these trends are indicative of aromatic carbon increases with charring temperature. Zhang et al. (2011) measured increases of aromatic C from 37 to 43% as pyrolysis temperature was increased from 350 °C to 700 °C. The difference in surface area between the BC700, BC350, and WC400 would also likely have had a strong impact on pendimethalin dissipation. In the case of BC700, char increased pendimethalin persistence.

3.4. Metribuzin dissipation products

Of the three metribuzin degradate products, only DA was detected in soil extracts (Fig. 4). The compound was detected in all treatment combinations. More DA was detected in the silt loam soil than the clay or the loamy sand. In the silt loam system, DA was detected as high as 0.78 $\mu g\,g^{-1}$ soil. Silt loam amended with BC350 had the lowest levels, and the control exhibited intermediate levels of DA. This supports the higher DT_{50} for metribuzin in the BC350 amended soil. For the clay soil, formation of DA in both the control and BC700 were similar, but about 50% lower than in the silt loam. The clay + BC350 DA level was lower, about 3X, compared to the control. For the sand soil, WC400 also appeared to slow formation of DA. The conversion of metribuzin to DA was about 5–10%, similar to values reported elsewhere (Henriksen et al., 2004). Considering that no DADK was observed, the DA formed was relatively stable. The compound had a similar DT_{50} in topsoil as metribuzin, 29 and 32 d, respectively (Henriksen et al., 2004).

3.5. Pesticide efficacy trial

In the Tifton loamy sand, palmer amaranth emergence was about 50% in the no biochar control (Fig. 5). At the 1–4% biochar rate a trend of increased palmer amaranth emergence was observed, and at the 8% rate palmer amaranth emergence was statistically higher than the control ($p = 0.072$). At the laboratory study rate of 2%, the WC400 biochar significantly increased pendimethalin DT_{50} (Table 4). Thus is it possible that reduced pendimethalin activity due to the biochar addition led to increased weed seed germination. It is also possible that the biochar improved soil conditions, such as water holding capacity, aeration, or reduced bulk density, and facilitated improved germination. Solaiman et al. (2012) observed biochar rates as high as 20 $Mg\,ha^{-1}$ improved wheat (*Triticum aestivum* L.) seed germination in soil/biochars mixtures, however increases were relatively small (5 to 9%) and mechanisms were not identified. On the other hand, Quilliam et al. (2012) showed similar weed seed emergence at control, 25, and 50 $Mg\,ha^{-1}$ rates of biochar added to field soil. But cumulative weed biomass was significantly reduced by about 50% due to reapplications of fresh biochars. In the current study, palmer amaranth

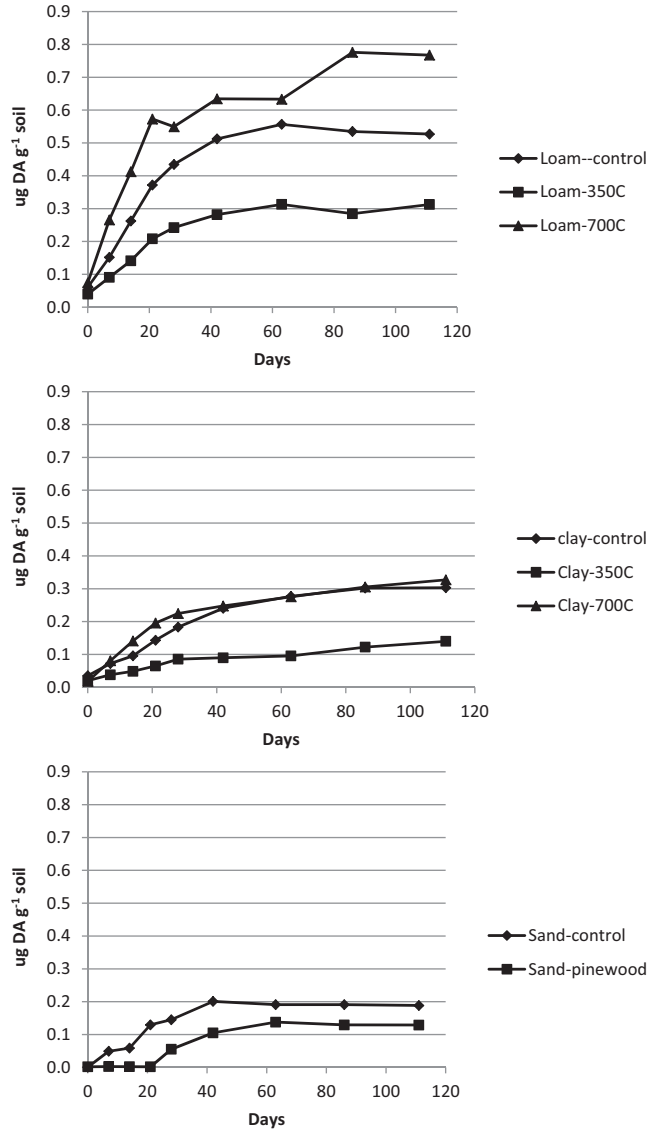


Fig. 4. Desamino-metribuzin (DA) formation in (A) silt loam soil, (B) clay soil, and (C) sandy soil with and without biochar as indicated during the laboratory incubation study. Points are means of 3 replicates.

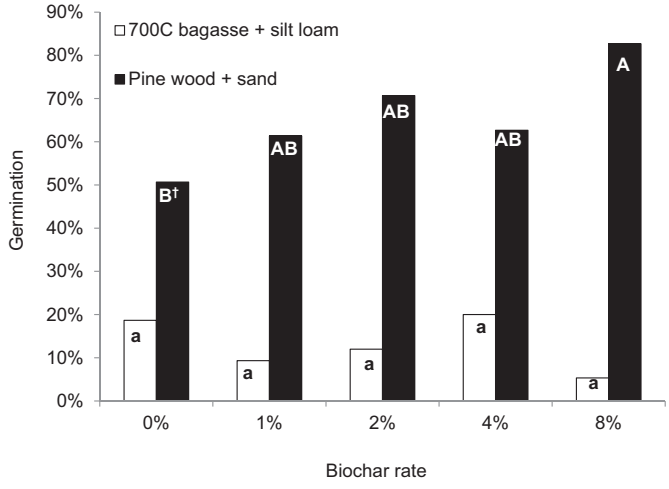


Fig. 5. Effects of biochar and herbicides on the germination of Palmer amaranth seeds in either Louisiana silt loam or Georgia sand soil. †Bars followed by the same uppercase or lowercase letter are not statistically different at the $p < 0.10$ level of significance.

Table 5
Soil organic carbon (SOC) concentrations following biochar additions.

Soil	Biochar	SOC (%)	Increase (fold)
LA silt loam	control	0.85 E[a]	–
	350 °C bagasse	2.00C	2.4
	700 °C bagasse	2.11C	2.5
LA clay	control	1.26 D	–
	350 °C bagasse	2.41 B	1.9
	700 °C bagasse	2.77 A	2.2
GA sand	control	0.77C	–
	pine wood	2.41 B	3.1

[a] Means followed by the same letter are not different ($p < 0.05$).

germination in Cancienne silt loam soil was consistently ≤20% (Fig. 5). There were no statistical differences between any rate of biochar addition on palmer amaranth emergence ($p = 0.277$). A post-experiment check showed low levels of both pendimethalin (0.22 μg g^{-1}) and metribuzin (0.33 μg g^{-1}) in the silt loam soil, thus it is possible some residual activity as well as the fresh chemicals applied was enough to reduce germination at any biochar rate. It is also possible that the higher SOC and clay minerals in the silt loam quenched biochar impacts on herbicides. Neither test proved conclusively that biochar can negatively impact herbicide efficacy strongly (Table 5)

Generally biochar has been observed to reduce the efficacy of soil-applied herbicides. This is typically linked to increased herbicide sorption in biochar amended soil. The assumption is that sorption reduces bioavailability; however the extent to which "bioavailability" is reduced appears to be linked to herbicide mode of action. For example Nag et al. (2011) found that biochar additions to soil decreased activity of atrazine more than trifluralin even though trifluralin is sorbed more strongly by soil and biochar. Trifluralin acts through direct contact of root tips of germinating seeds. Plant uptake is not required and presumably biochar-sorbed trifluralin retains some of its activity. In contrast atrazine is a photosynthesis inhibitor. Its action involves dissolution in soil solution, uptake by plants, and translocation to leaves where photosynthesis inhibition takes place. The herbicides used in our study were comparable in that pendimethalin is a dintronitroaniline like trifluralin, is strongly sorbed, and acts by direct contact with root tips. Metribuzin, like atrazine, is a triazine photosynthesis inhibitor that acts through plant uptake from soil water. In sum, biochar does generally decrease herbicide efficacy but impacts depend on whether or not herbicides must be taken up plants to exhibit toxic action. Herbicide sorption by biochar reduces aqueous concentration. In turn plant uptake is reduced. Thus impacts are greatest on herbicides whose activity requires plant uptake.

4. Conclusions

Biochar additions affected metribuzin and pendimethalin dissipation in agricultural soils differently. For metribuzin, BC350 doubled the DT_{50} in the silt loam soil from 25 to 57 d, but only increased DT_{50} in the clay soil from 57 to 74 d. For metribuzin, WC400 increased the DT50 from 28 to 39 d, despite the very small surface area (0.5 m^2 g^{-1}). For pendimethalin, BC700 increased DT_{50}'s in silt loam (from 23 to 54 d) and clay soils (from 22 to 52 d). Sorption parameters for Freundlich and linear isotherms were higher for BC350 (2-3X) and BC700 (4.7–14X), when compared to WC400. The only degradate identified was DA, and its formation was linked to metribuzin dissipation. In the Tifton loamy sand, high rates of biochar (8% by weight) increased Palmer amaranth germination. However, little impact on germination was observed in the Cancienne silt loam soil at any biochar rate. Despite the potential advantages for soil health, the change in DT_{50}, coupled with possibly herbicide efficacy concerns, should be considered when

applying biochars in these agricultural soils. Soil, biochar, and herbicide properties will all need to be taken into account to determine the impact biochar will have on agronomic practices.

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